Growth of ZnO Nanowire and Its Application as UV Photodetector

Thesis submitted in partial fulfilment of the requirements for the award of the degree of

MASTER OF SCIENCE

By

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CERTIFICATE

This is to certify that the work in the report entitled "**GROWTH OF ZINC OXIDE NANOWIRES and ITS APPLICATION as UV PHOTODETECTOR**" by Archana Tiwari, in partial fulfilment of Master of Science degree in PHYSICS at National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance. The work is satisfactory to the best of my knowledge.

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ABSTRACT

Zinc Oxide (ZnO) nanostructures with their significant properties have various application in optoelectronics, sensor devices and energy conversion devices. This report includes deposition of ZnO film by rf reactive sputtering on glass substrate. Its analysis using XRD, FESEM and UV-VIS spectroscopy to study its morphology, crystal structure, band gap and transmittance. Further, the deposited film is taken as substrate for the growth of ZnO nanowires using Hydrothermal Method. Various parameters affecting the growth conditions like growth temperature, growth time, and precursor concentration have been studied and optimizations of reaction conditions are done. Analysis of the samples fabricated under different conditions is carried out using XRD and FESEM characterization techniques. Zinc oxide nanowires have their application as UV photodetector due to their wide band gap and high surface to volume ratio. To enhance the absorption ability, carrier concentration and photoresponse, Zinc Oxide nanowires surface is functionalized using Poly(vinyl alcohol) for the application of UV photodetector. Photoresponse and sensitivity is studied for both coated and uncoated, using I-V characterization. To analyse optical switching action under the illumination of UV light photoresponse of these nanowires is plotted with respect to the time.

Keywords: Zinc Oxide, Thin film, Nanowires, Hydrothermal Method, Polymer Functionalization, UV Photodetector

CONTENT

CHAPTER – 1

INTRODUCTION

The significantly different physical properties of nanostructured materials in comparison to their bulk counterpart made them important as widely used material in the field of science and technology. The change in physical properties lies in their characteristic structural features in between the isolated atoms and the bulk macroscopic materials. On atomic level, there is a change in band structure due to quantum confinement, which is due to the changes in the atomic structure resulting from the direct influence of the ultra-small length scale on the energy band structure. The significantly important electronic, mechanical, optical and magnetic properties of the nanoscale materials can be attributed to the changes in the total energy and band structure of the system resulting from the confinement in particular dimension. Materials in nano dimension have their properties more influenced by surface interaction than their bulk part; an increase in surface to volume ratio ensures more effective surface phenomena.

Nanowire is one of the nanostructured material which has its length confined in one dimension. They are characterized by very high aspect ratio, length lies in micrometre range and diameter in nanometer range. Nanowires can be taken as model system to study influence of dimensional confinement on the optical, magnetic, electrical and mechanical properties of a material. ZnO nanowires have their application in optoelectronic and energy conversion devices.

Zinc oxide has been widely studied since 1935 [1]. It is an important II–VI compound semiconductor material having optical and electrical properties which can be used in a number of applications, like high transmittance conductive oxide coatings for solar cells, gas sensors, chemical sensor, UV photodetectors, and bulk acoustic wave resonators. It has wide direct band gap energy of 3.37 eV, making it transparent for visible light and operates in the UV to blue wavelengths. The exciton binding energy is 60 meV for ZnO; the higher exciton binding energy enhances the luminescence efficiency of light emission and make sure that excitonic transition is less affected by thermal energy. ZnO has exhibited better radiation resistance for possible devices used in space and nuclear applications. ZnO is an amphoteric oxide having isoelectric point of 9.5 which can be grown on inexpensive substrate, such as glass, at relatively low temperatures. It is bio-safe and biocompatible. ZnO nanostructures, such as nanowires and nanorods are ideal for

detection applications due to its large surface area to volume ratio. ZnO nanowires and nanorods are attractive components for nanometre scale electronic and photonic device applications because of their unique chemical and physical properties. A wide variety of nanodevices including ultraviolet detectors, sensors, field effect transistors, Schottky diodes, intramolecular p– n junction diodes and light emitting device arrays have been fabricated utilizing ZnO nanorods (nanowires) [2]. Owing to its application synthesis of ZnO nanostructures is currently attracting intense worldwide interest. ZnO have a piezoelectric tensor equal to or even greater than that of GaN and AlN which means that ZnO is a suitable candidate for device applications requiring a large electromechanical coupling. The thermal conductivity, *'κ'* of a semiconductor is an important property when considering high-power/high temperature devices. It is a kinetic property affected by the vibrational, rotational and electronic degrees of freedom, and is predominately limited by phonon-phonon scattering in a pure crystal. ZnO, like most other semiconductors, contains a large number of point defects, which have a significant effect on the thermal conductivity. It has wide industrial application due to the development of growth technologies for the synthesis of high quality single crystals and epitaxial layers which allows the realization of ZnO-based electronic and optoelectronic devices. Improvements in growth technology of ZnO nanostructures, epitaxial layers, single crystals, nanowires and nanoparticles, ZnO devices have large potential to be increasingly functional in the near future.

Physical Properties of ZnO [1]

Molar Mass	81.409gm/mol
Appearance	White solid
Odour	Odourless
Density	5.606gm/cm
Melting point	19750 ºC (Decomposes)
Boiling Point	23600ºC
Solubility in water	0.16mg/100ml(30ºC)

Band gap	3.37 eV (Direct)
Refractive Index	2.00

Crystal Structure of ZnO:

Most of group 12–16 binary compounds crystallize in the form of cubic rock salt or cubic zinc blende structure or hexagonal wurtzite structure. The rock salt structure is that of common table salt which may be obtained at very high temperature and pressure. In normal ambient conditions the wurtzite symmetry is thermodynamically favoured over the zinc blende [1]. In both the cases, each cation is surrounded by four anion arranged in four corners of a regular tetrahedron with the cation at the center. Similarly, four cations surround each anion. Zn-O bond possesses good ionic character which is reflected in its band gap. This tetrahedral coordination gives rise to polar symmetry. However what distinguishes the wurtzite structure from the typical zinc blende structure is its rotation symmetry along <111 > direction, in wurtzite structure the successive tetrahedrons are on top of each other and in zinc blende structure they are not aligned. The wurtzite structure has hexagonal unit cell structure with two lattice parameters a=3.2495 A and c=5.2069 A. The measure of the amount by which each atom is displaced with respect to next along the c-axis is given by the parameter u, and experimentally, zinc oxide wurtzite structure is found to have u= 0.38 [1].

There is lot of work available on growth of one dimensional zinc oxide nanostructures. A few applicable methods to grow nanomaterials include wet chemical method, metal organic chemical vapour deposition, pulsed laser deposition, molecular beam epitaxy and even top-down approaches by etching. Among all the above method, wet chemical method is comparatively attractive for several reasons – they are low cost, less hazardous, and capable of easy scaling up; the growth occurs at comparatively low temperature, compatible with flexible organic substrate, metal catalyst is not needed and there are number of parameter can be tuned to effectively control the morphology and properties of final product [3]. Nanowires grown in my work follows wet chemical synthesis-

the hydrothermal method because it does not require any specialized equipment and it is very cheap and easy to do. This method if does not provide uniformity, is very much economic.

In present work zinc oxide nanowires are grown on glass substrates with seeded layer of ZnO crystal as the study of optical properties could be best done on a substrate that is transparent. The growth of nanowires on glass substrate has been studied by varying reaction parameters like temperature, concentration and time. The main advantage of zinc oxide nanowires over others in same fields is the wide band gap of zinc oxide which can be utilized in various electronic devices. Functionalization of nanowires surface is carried out using poly(vinyl alcohol) (PVA) for application of UV photodetector.

CHAPTER 2

REVIEW OF CONTEMPORARY WORKS

The research on ZnO started around in the 1930s due to its prospects in optoelectronics applications owing to its direct wide band gap E_g 3.37 eV at 300 K. Zinc oxide nanostructures have been fabricated and proven versatility and compatibility in numerous applications. ZnO nanostructures were synthesized in the form of nanorods, nanowires, nanotubes, nanobelts, nanocombs, nanosprings, nanorings, nanobows and nanopropellers, etc.

ZnO has attracted scientific community because of its variety of application which comes from following properties :

- It has a direct wide band gap of 3.37 eV
- It has a large exciton binding energy of 60 meV
- It can have near UV emission and transparent conductivity
- Its exceptional piezoelectric property resulting from low symmetry of wurtzite structure of ZnO
- It is biological safe and compatible

There are various methods available to grow ZnO nanowires like metal organic chemical vapour deposition, wet chemical method, pulsed laser deposition, molecular beam epitaxy. Wet chemical method being low cost, easy scaling, and low temperature method is choice of various research groups. Few of the research work going across the globe regarding ZnO nanowires are following –

Sheng Xu and Zhong Lin Wang [5] in their review on one dimensional nanostructures provide a comprehensive overview of the progress made in the growth of 1D nanostructures via wet chemical method. They have detailed about the synthetic methodologies, corresponding growth mechanisms, various nanostructures grown, position-controlled growth on substrates and their doping and alloying. This paper also provides a review for 1D nanostructures with their functional properties in catalysis, hydrophobic surface modification, sensing, and electronic, optical, optoelectronic, and energy harvesting devices.

Yu et al. [6] reported about the effect of precursor concentration, pH, growth temperature and growth time on size and density of ZnO nanowire arrays (ZNAs), showing that nanowires of

desired size can be grown by simple variation in growth parameters. Further they have made a point about the transparency of ZNAs which can useful for photovoltaic and other optoelectronic applications.

Jorge L. Gomez, Onur Tigli [7] in their report on ZnO nanostructures gave a comprehensive review on the growth methods currently employed in research, industry, and academics. Methods examined include: vapor–liquid– solid, physical vapor deposition, chemical vapor deposition, metal–organic chemical vapor deposition, and hydrothermal-based chemical approach. Each of these methods is discussed with their strengths and weaknesses and analyzed with objective comparison metrics.

Lori E. Greene and group [8] have discussed the method for the growth of vertical ZnO nanowires on any arbitrary substrate using vapour phase or liquid phase approaches.They have formed a thick layer of textured ZnO nanocrystals with their c -axes normal to the substrate by the decomposition of zinc acetate at 200-350°C to provide nucleation sites for vertical nanowire growth and is critical for the growth of nanowires.

Greene et al. [10] reviewed two strategies to grow ZnO nanowires from Zn salt in aqueous and organic solvent. Nanowires can be grown in aqueous medium of Zinc Nitrate and Hexamethylenetetramine (HMT). They have further reported an increase in length and aspect ratio on addition of poly(ethylenimine) and vertically alignment NWs can be achieved by nucleating nanowires from oriented ZnO nanocrystals.

J.G. Lu et al. [11] provide a comprehensive review focussing on quasi one dimensional nanostructures of metal oxide and their physical properties. They have detailed about the various vapour phase and liquid phase growth available to form one dimensional nanostructures. They have also discussed about the characteristics of a number of metal oxide like ZnO, SnO_2, TiO_2, In_2O_3, Ga_2O_3 etc. and their optical, mechanical, magnetic, electrical and chemical sensing property. Applications based on study of important features of metal oxides are also highlighted in this work.

S. Xu et al. [13] have given a seedless approach for density controlled growth of ZnO nanowires on catalysing the reaction process by depositing a thin layer of Au on the substrate. They have shown controlled density can be achieved by changing the precursor concentration. Effect of growth temperature and time is also investigated in their work. Further they have noted that by following the given approach nanowires can be grown on variety of substrates like glass, polymer, metal, semiconductor given a smooth surface of the substrate. Nanowires grown with this technique

have their application in field effect, vertical field effect transistor arrays, nanogenerators, nanopiezoelectronics.

Lori E. Greene, Peidong Yang and group in their paper on "Low temperature wafer scale production of ZnO nanowire arrays" [15] noted that hydrothermal method of growth of nanowires gives homogeneous and dense array of nanowires on a number of substrate. They have noted seeded layer of ZnO crystal is critical for nanowire growth and growth of nanowires is substrate independent. Effect of growth time on morphology and density of nanowires is also studied. Dependence of visible luminescence on annealing temperature and presence of O_2 during growth is put into discussion.

In general, above references have discussed about the various growth mechanism employed for growth of nanowires, characteristics of each mechanism, advantages of wet chemical method over other available methods. Hydrothermal method one of the wet chemical method have put into discussion in a few reviews. Considering the growth mechanism of nanowires, dependence of morphology, aspect ratio, density of nanowires arrays on precursor concentration, pH, growth temperature, growth time is also discussed in detail.

As my work involve, applicability of ZnO nanowire as UV photodetector by carrying out surface functionalization of as grown nanowires which causes increase the sensing property, UV absorption ability and other parameters involving efficient detection. Reviews of various works on sensing properties of ZnO nanowires are following:

In a research paper "Nanowire Ultraviolet Photodetectors and Optical Switches" [13] photoresponse of ZnO nanowires have been discussed based upon illumination power, wavelength and bias voltage. General mechanism for the UV sensing is also discussed in this paper.

Chang Shi Lao, Zhong L. Wang and group in their research paper "Giant Enhancement in UV Response of ZnO Nanobelts by Polymer Surface-Functionalization" [16] observed the effect functionalization from a number of polymers, namely, Polystyrene Sulphate (PSS), Poly(styrene-co-maleic acid) (PS-Co-MAC), Poly(N-isopropylamide) (PNIPAM), Carboxymethyl Cellulose (CMC), on the absorption of UV light and sensing property. They have found that PSS coated NBs have high UV absorption near ~ 280 nm compared to other polymers. They have concluded that

high selectivity of functionalized ZnO nanowires for UV detection is due to the presence on oxygen related hole trapping states at the NW surface.

Ashok Bera and Durga Basak in research paper [17] have given the effect of surface functionalization by Poly(vinyl alcohol) (PVA) on the ZnO nanowires grown by aqueous chemical method. PVA acts as a barrier for O_2 reduces the width of depletion layer on the surface of ZnO hence reduces the surface trapping of the charge carriers.

CHAPTER 3

ZnO - Thin Film and Nanowires

There are various types of nanostructures playing a vital role in the development of science and technology. Thin films are of importance as they provide large surface interaction, less consumption of material, less power consumption, are light weight and portable, material property can be varied in wide range, can be easily doped and patterned in micrometer range. A few methods to deposit thin films are Physical Vapour Deposition, Chemical Vapour Deposition, Molecular Beam Epitaxy, and Pulsed Laser Deposition. Sputtering which comes under Physical Vapour Deposition have advantage compared to other methods as it gives good film quality, less wastage of material, low cost methods for growth thin film.

3.1 Thin Film

3.1.1 Chemical Vapour Deposition (CVD)

Chemical Vapour Deposition (CVD) technology is interesting as it gives rise to high-quality films and applicable to large-scale production. In the CVD method, precursors are introduced

inside the chamber by carrier gases or in gaseous phase, they made to flow through a nozzle towards the substrate where they react to give a deposited film on the substrate. This is comparatively a high temperature deposition method. Plasma enhancing and light photons can be used to provide required activation energy for the reaction and hence can occur at comparatively low temperature. ZnO deposition occurs as a result of chemical reactions of vapour-phase precursors on the substrate, which are introduced into the growth zone by the carrier gas. Metals can be injected into the surface with their in the form of their organic compound like to introduce Zn, Diethylzinc can be used which has a boiling point of 117ºC The reactions take place in a reactor where a necessary temperature profile is created in the gas flow direction. [4]

3.1.2 Pulsed Laser Deposition (PLD)

Pulsed laser deposition uses a pulsed laser of high power to irradiate a target surface. On irradiating the target surface, target surface sublimes to eject its atoms. These atoms acquire a directional flow towards the substrate surface and get condensed on the substrate surface. Advantage of a PLD system is it maintains the stoichiometry of the compound, gives good film quality, and gives a film of high purity. But it has a demerit of low area deposition. The quality of the grown film depends on the substrate temperature, ambient gas condition and intensity of the laser used.

3.1.3 Molecular Beam Epitaxy

This method is ultra-high vacuum based method which gives highly crystalline epitaxial layer. In this method source is made to sublime inside the effusion cell and then a directional flow is made towards the heated substrate in very controlled manner. It has a slow deposition rate with frequent shuttering. Thin film grown by this method have high purity so this also requires a highly pure source material. It has an advantage of in-situ analysis for the modulation of each grown layer using RHEED (Reflection High Energy Electron Diffraction) and RGA(Residual Gas Analysis) to maintain cleanliness of the chamber.

3.1.4 Sputtering

Sputtering involves ionization of an inert gas under the effect of high potential applied across the electrodes. At breakdown potential of sputtering gas, it ionizes into ions and electron, ions under the effect of electric field move towards the cathode (target) to collide with target surface causing removal of target atom from the surface of target with other species like reflected neutrals, ions, secondary electrons etc. Due to momentum transfer between target atom and sputtering ion, ejected target atom attains a directional velocity towards the substrate and get deposited on the substrate surface. Power supplied in sputtering can be of dc or rf type. DC power supply having low cost have demerits of target poisoning and not applicability for the insulating target, whereas, rf sputtering having relatively high cost can ensure better film quality and applicable to all kind of targets (metal, semiconductor, insulator). In case of reactive sputtering, where a reactive gas is made to flow inside the chamber, reacts with the target material to form compound on the substrate surface, for which substrate heating is provided.

3.2 Nanowires

There are two basic approaches to synthesize nanowires –

1. Top-Down
2. Bottom-Up

Top down approach reduces a large piece of a material to small pieces, by means of lithography or electrophoresis to form nanowires. Bottom-Up approach synthesizes nanowires by combining constituents adatoms.

3.2.1 Hydrothermal method

ZnO nanowire arrays can be made in aqueous solutions, using two-step process.

- Preparation of ZnO seeds on desired substrate
- Growth of nanowires on seeded substrate

ZnO seed layer can be prepared by any thin film deposition technique, namely, sputtering, spin coating or dip coating. After preparing the thin film on the substrate, it is placed in equimolar solution of Zinc Nitrate ($Zn(NO_3)$) and Hexamethylenetetraamine (HMT) such that the coated surface directly faces the solution. Reaction is kept at 90^{o}C for around 4-8 hours. After some

time solution turns milky indicating the formation of white precipitate of Zinc Oxide. With the end of growth time, substrate is taken out of the solution and rinsed slowly in De-ionized water to remove any loosely adsorbed layer. Then it is kept for drying at room temperature.

Reaction Mechanism –

$$(CH_2)_6N_4 + 6\,H_2O \longrightarrow 6\,HCHO + 4\,NH_3$$

$$NH_3 + H_2O \longrightarrow NH_3{\cdot}H_2O$$

$$NH_3{\cdot}H_2O \longrightarrow NH_4^+ + OH^-$$

$$Zn^{2+} + 2\,OH^- \longrightarrow Zn(OH)_2$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

Role of HMTA –

In the formation of nanowires HMTA acts as a weak base and plays most fundamental role for the growth of ZnO nanowires. It slowly hydrolyze in water solution to produce OH^- ion and this OH^- ion is important to precipitate out Zn^{2+} ion in high pH environment. The solution medium having a pH 7-8 is supposed to be good for the proper growth of nanowires.

When used as substrates for epitaxy, proper surface preparation is necessary to evaluate the quality of hydrothermally grown ZnO. In order to reduce the strains and dislocation density in epitaxial ZnO and related films, closely lattice matched substrates are favoured for growth. Also with seeded ZnO layer the texturing of nanowires results from a thermodynamically controlled nucleation and is independent on its interaction with the substrate. [11]

3.3 ZnO as UV Photodetector

ZnO nanowires due to their wide band gap of 3.37 eV, wide range of photoluminescence emission band from blue to yellow, high quantum yield and stability of its nanoparticles in aqueous solution for biological labelling can be used as UV sensors.

Ideal properties of a UV sensors are as follows:

- Fast Response time
- Small reset time

- High selectivity
- High responsivity
- Good signal to noise ratio

UV sensing Mechanism

As ZnO is an n-type semiconductor, O_2 molecules from environment get adsorbed on nanowires surface forming a depletion layer with low conductivity near the nanowires surface.

$$O_2\,(g) + e^- \longrightarrow O_2^-\,(ad)$$

Upon exposure to the UV light there be production of e^- - hole pair, holes will migrate to the surface of nanowires which has negatively charged oxygen molecule while electrons can move through the bulk part with less chance of recombination hence increasing the photo current.

Properties of ZnO nanowires as UV photodetector [13][14]:

- Conductivity of ZnO nanowires is highly sensitive to the exposure of UV light.
- Photoresponse is linearly dependent on power of illumination.
- It has excellent wavelength selectivity.
- Large photo response can be detected at higher bias voltage.
- Response cut-off wavelength is found to be ~ 370 nm.
- Thinner nanowires have more sensitivity.
- Photoresponse dependence on the ambient gas conditions.
- ZnO nanowires have limited UV sensibility due to presence of point defects and confined dimensionality.

Change in charge transport mechanism on functionalization:

Free electron inside the nanowire may get trapped by the positively charges PDADMAC surface. On UV illumination these localized electrons can trap photo-generated holes and reduces e^- - hole recombination rate and hence increases the carrier life time. Due to this electron conduction takes place in the bulk of the material while recombination takes place at the surface of the material hence increases photo-conductance.

In case of PVA coating, PVA acts as O_2 barrier and reduces the thickness of depletion layer on the surface of nanowire hence reduces the trapping of carrier charges on the surface of nanowire. Releasing more available carrier for photoconduction and, therefore, gives better photoresponse.

CHAPTER 4

CHARACTERISATION TECHNIQUES

4.1 X-Ray Diffraction

4.2 Field Emission Scanning Electron Microscopy

4.3 UV/VIS Spectroscopy

4.4 I-V Measurement

4.1 X-Ray Diffraction

This method gives the information about the crystalline nature of the sample which includes miller indices, crystal structure, phase composition, nature of sample (amorphous or crystalline). In this method X rays are made to fall on the sample if the falling X rays satisfies the Bragg's condition they gets diffracted from the sample. Intensity of diffracted X ray is plotted with respect to scattering angle. Higher intensity ensures more number of atoms lies in that particular plane. This technique can also be used to study change in crystal structures in various experimental conditions like thermal distortion.

Determination of crystal size:

The X-ray diffraction analysis in one of the most applicable method for the estimation of crystallite size in nanomaterials. The broadening of the Bragg peaks contains the development of the crystallite refinement and internal stain. To size broadening and stain broadening, the full width at half maximum (FWHM) of the Brag peaks as a function of the diffraction angle is analysed. Crystallite size of the deposits is calculated by the X- ray diffraction (XRD) peak broadening. The diffraction patterns are obtained using Cu K_α radiation. The grain size can be estimated the Scherrer equation

$$D = \frac{0.9\,\lambda}{\beta\, Cos\theta}$$

where, λ : is wave length of X-ray, β is FWHM in radian, θ is peak angle.

4.2 Field Emission Scanning Electron Microscopy

It is one of the widely used methods for material characterization specially to study their morphology and topological features. This method utilizes emission of electron from a cathode when high potential is applied across its end. This electron beam accelerated through a high potential and attains high momentum causing reduction in its wavelength and according to the

Rayleigh criteria provide high resolution image of the sample under investigation. Electron beam is made to pass through a set of electromagnetic lenses to focus properly on the specimen surface. Interaction of electron with the specimen can result in secondary electrons, backscattered electrons, Auger electrons etc to come out of the sample carrying various kind of information. Detection of secondary electron is most common mode of detection, as they have low energy and originated from a few nanometres of the surface. it is detected by scintillator or photomultiplier tube. This gives information about the surface morphology of the specimen. Backscattered electrons are high energy electrons resulting from the reflection or backscattering from the volume of specimen. As they comes from the comparatively more depth inside the specimen, they carry information about the topology of the specimen, change in specimen property with the depth can also be analyzed with detection of backscattered electrons.

Following information can be extracted from FESEM analysis :

- Use of field emission results in improved spatial resolution, less damage of the specimen surface and minimized surface charging. It can be give following information about the specimen surface
- It can also be used for the cross section analysis of the semiconductor device for gate width, gate oxide, film thickness and construction details
- It can derive information about structure uniformity determination and advanced coating thickness
- Elemental composition measurement and contamination feature of the geometry.

4.3 UV-VISIBLE Spectroscopy

UV visible spectroscopy uses wavelength ranges from UV to visible range to study transmittance, reflectance, and absorbance of the material under investigation. It can be used to find information about the band gap of a deposited semiconductor film.

UV/Vis spectroscopy is often find its application in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds because of following :

- Transition metal ions shows color because they have vacant d orbitals in which an electron can make transition by absorbing radiation in visible range and come back to original state by emitting a radiation.
- Organic compounds having high degree of conjugation can also absorb light in UV- VIS range in this case the solvent plays an important role e.g. ethanol shows weak absorption for most of the wavelengths. Solvent polarity and pH is important while taking absorption spectrum of the organic compounds.

Band Gap of a semiconductor can be measured using UV-Visible spectroscopy by following relation –

$$(\alpha h\nu)^{1/n} = B\,(h\nu - E_g)$$

α : Absorption Coefficient = -log(T)/(d)

T = Transmittance, d = Thickness of the film

n = 2 Indirect band Gap, ½ Direct Band Gap

B = Constant related to transition probability

UV-Visible spectroscopy is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer-Lambert law:

$$A = -\log_{10}(I/I_0) = \varepsilon.\ c.\ L$$

Where, A = Measured Absorbance

I_0 = Intensity of Incident Light

I = Transmitted Intensity

L= Path Length through the sample

c=Concentration of Absorbing species

I-V Measurement

I-V characteristic of a circuit shows the impedances of a circuit and the junction property of a contact. It can be measured by making contact on the semiconductor surface. In case of Ohmic contact, it has a linear relation but in case of Schottky contact there is non-linear behaviour for I-V curve. It is one of the basic instrument to quantify electrical properties of an instrument and analyse the characteristics of number of instruments which include semiconductors, MOSFETs and junction properties like Metal-O-Semiconductor and Metal-Oxide-Metal etc.

CHAPTER 5

SYNTHESIS OF ZnO NANOSTRUCTURES

5. FABRICATION

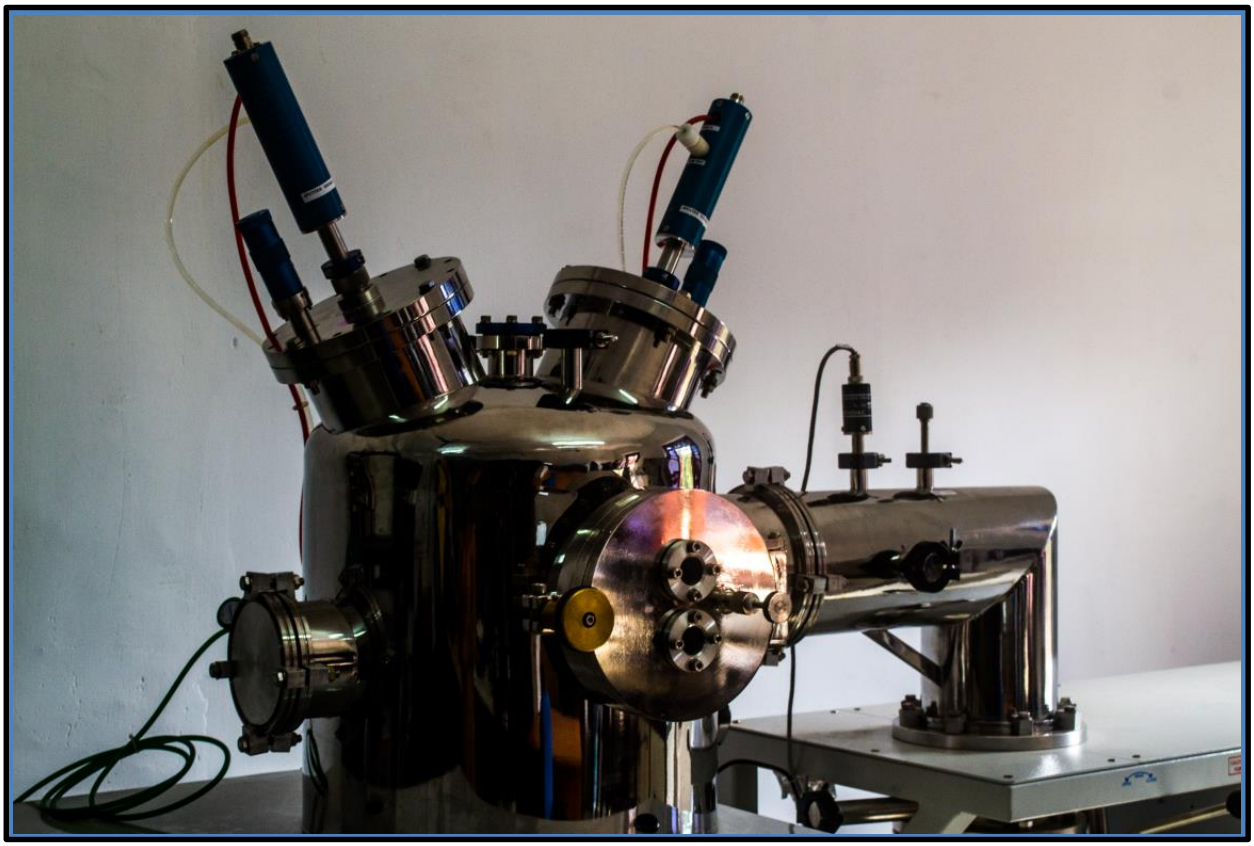
Fabrication of any thin film or nanostructure requires a substrate. In this work for the deposition of thin film and growth of nanowires glass substrate is taken. Glass substrate is used because of its low cost, stability upto a growth temperature of 400 ºC, favourable for large area deposition, easy availability, insulating in nature, transparent and smooth surface. Before putting the glass substrate for deposition it needed to be cleaned, to remove any foreign contaminants. Glass cleaning involves following procedure:

1. First clean the glass slide using soap solution.
2. Sonicate it in Acetone for 10 minutes and then rinse with DI water.
3. Sonicate it in IPA (isopropyl alcohol) for 10 minutes and rinse with DI water.
4. Dry the cleaned glass substrate.

5.1 Growth of ZnO thin film by Sputtering

RF magnetron sputtering is employed to grow Zinc Oxide thin films. Thin film is grown by reactive sputtering using Zn as target material and O_2 as reactive gas. To start with RF sputtering method, first pure (99.999 %) ZnO target is fixed at the cathode and cleaned glass substrate is

loaded on the anode electrode. Target and substrate distance is kept fixed at 10 cm then chamber is closed. To remove unwanted gases and moisture high vacuum of 8.5×10^{-7} mbar is obtained using Diffusion Pump with Rotary Pump acting as forepump and backing pump. After running the set up for around one hour desired vacuum is achieved. Then Ar and O_2 gas is made to flow inside the chamber maintain Ar to O_2 the flow ratio of 2:3, with partially closed high vacuum valve. Working pressure inside the chamber is kept constant at 8×10^{-3} mbar. For the proper bonding between the Zn and O at the substrate surface is maintained at 200ºC. RF power of 150 W is applied to the electrodes and film is deposited for 30 minutes. After 30 minutes chamber is left for cooling for around 30 minutes and then substrate with deposited film is taken out of the chamber.



RF Magnetron Co-Sputtering Unit, Electronic Materials and Devices Laboratory, Department of Physics NIT Rourkela

Deposition mechanism

High RF power of frequency 13.56 MHz applied inside the chamber, ionizes the gas molecules, these ions moves inside the chamber under the effect of oscillating RF electric field. These ions in their collision with target eject the target atoms due to momentum transfer, target atom is ejected with other species like secondary ions, reflected neutrals, ions etc. This ejected target atom due to its directional momentum reaches to the substrate, loses its energy on substrate surface to get deposited. Substrate heating is provided in case of reactive sputtering so to reach the activation energy required to form Zn-O bond on the substrate surface and to achieve proper orientation. Continuing this procedure for 30 minutes a uniform thin layer of film is formed on substrate surface.

5.2 Synthesis of ZnO nanowires by Hydrothermal Method

In this method, equimolar concentration of Zinc Nitrate and Hexamethylenetetraamine (HMT) is taken by dissolving each reagent in 100 ml of DI water. This solution is kept inside a bottle and glass substrate with seeded ZnO layer is kept inside the bottle in such a way so that the deposited side faces downward inside the bottle. This solution is then heated at 90˚C for 4-8 hours. After some time depending upon the concentration and temperature of the reaction solution inside the bottle turns white showing the formation of zinc oxide. After the designated time sample is taken out of the bottle and rinsed slowly with DI water 2-3 times to remove any weakly adsorbed layer. Then it is kept for drying at room temperature.

Surface Functionalization

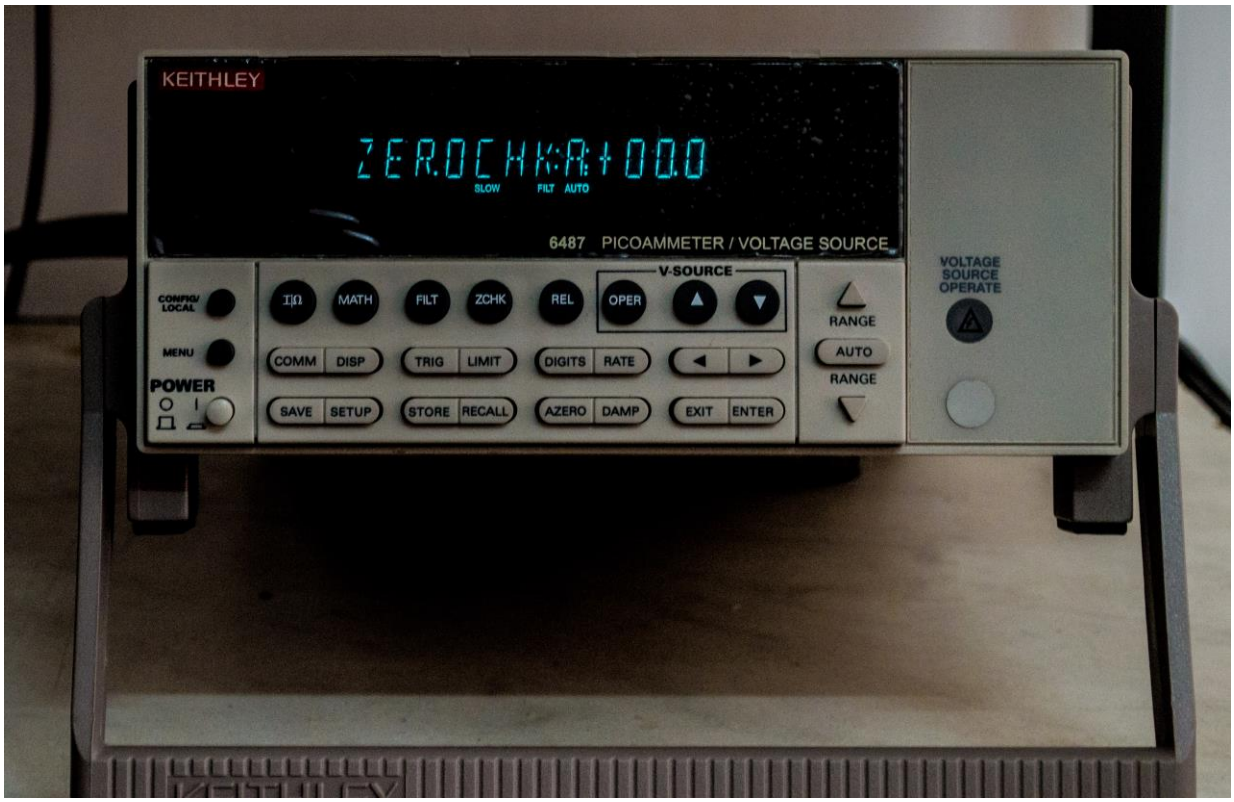
Surface Functionalization is done to enhance the surface property of a material for a particular purpose. There are a number of ways in which surface functionalization affects the surface interaction like it may increase the electron transport property and absorption ability, can cause surface band bending and reduction of surface trapping the charge carriers. On functionalization an extra energy state is introduced by the polymer which lies in the band gap and conduction band of ZnO this extra energy level acts as hopping state and increases the excitation probability

of electron to the conduction band [9]. Considering the application of ZnO nanowires for UV sensing two materials are used for surface modification:

Surface Capping by Poly(vinyl alcohol) [17]

- First as grown ZnO nanowires are taken.
- 0.2 gm of PVA dissolved in 50 ml of DI water at 80ºC for 2 hours.
- Then solution is kept at room temperature for one day to get uniform solution.
- As grown nanowires are dipped into the solution at 50ºC for one hour and then dried.

For the measurement of I-V characteristic of the polymer coated and uncoated nanowire sample contacts are made by masking the surface with mask having dot diameter of 1 mm and is put into thermal evaporation set up to form conducting dots of Aluminium film to measure the conductive property of the ZnO surface.



Picometer /Voltage Source , EMD Lab Dept. of Physics NIT- Rourkela

CHAPTER 6

RESULTS & DISCUSSION

6.1. ZnO Thin Film

6.1.1. Structural Characterization (X-Ray Diffraction)

6.1.2. Surface Morphology (FESEM)

6.1.5. UV-Visible Spectroscopy

6.1.7. Conclusions

6.2. ZnO NANOWIRES

6.2.1. X-Ray Diffraction

6.2.2. Field Emission Scanning Electron Microscopy

6.2.4. UV-visible spectroscopy

6.2.5. Conclusions

6.3. Functioalization and UV sensing

6.3.1 I-V Characteristic

6.1. ZnO Thin Film

6.1.1. Structural Characterization (X-Ray Diffraction)

X- ray Diffraction date shown in this report is taken from Rigaku Ultima IV diffractometer using Cu K_α-Radiation (λ=1.5418Å) ranging from $20^0<\theta<80^0$ at operating voltage of 40 kV and operating current of 40 mA.

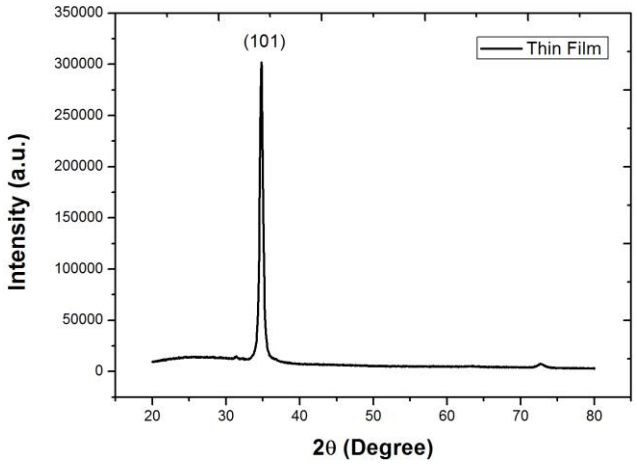


Figure 6.1.1 XRD pattern of the ZnO thin film deposited on glass substrate

- It is evident from the XRD pattern that deposited film have high crystallinity.
- Maximum peak intensity is obtained at 2θ value of 34.779º with corresponding interplaner distance d = 2.5773 Aº.
- Crystallite size is found to be around 14 nm
- A narrow peak is observed showing large crystallite size and good crystal quality.

6.1.2 Surface Morphology

FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM):

The morphology of the sample was observed in field emission scanning electron microscopy (FESEM) using NOVA NanoSEM 450 scanning electron microscope.

Thickness of the film is found to be 796.04 nm. It can be seen that surface of film have a uniform and smooth surface with large grain size.

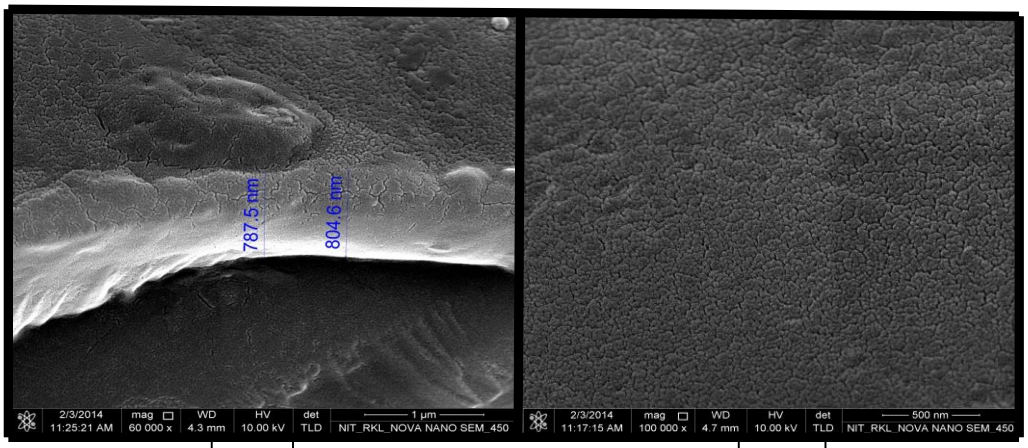


Figure 6.1.2 a) lateral view of the ZnO thin film b) Surface morphology of ZnO Thin Film

6.1.3. UV- Visible Spectroscopy

UV-Visible spectroscopy was performed to study optical properties of the thin film. The room temperature UV-Visible transmittance spectra was taken in the range of 200-800 nm is shown in the figure.

Band Gap Calculation :

$$(\alpha h\nu)^{1/n} = B\,(h\nu - E_g)$$

α : absorption Coefficient

n = 2 Indirect band Gap, ½ Direct Band Gap

B = Constant related to transition probability

- Band Gap (E_g) is found to be 3.26 eV.
- Sudden rise in transmittance at λ = 385 nm and it has high transmission coefficient for UVA to visible light.

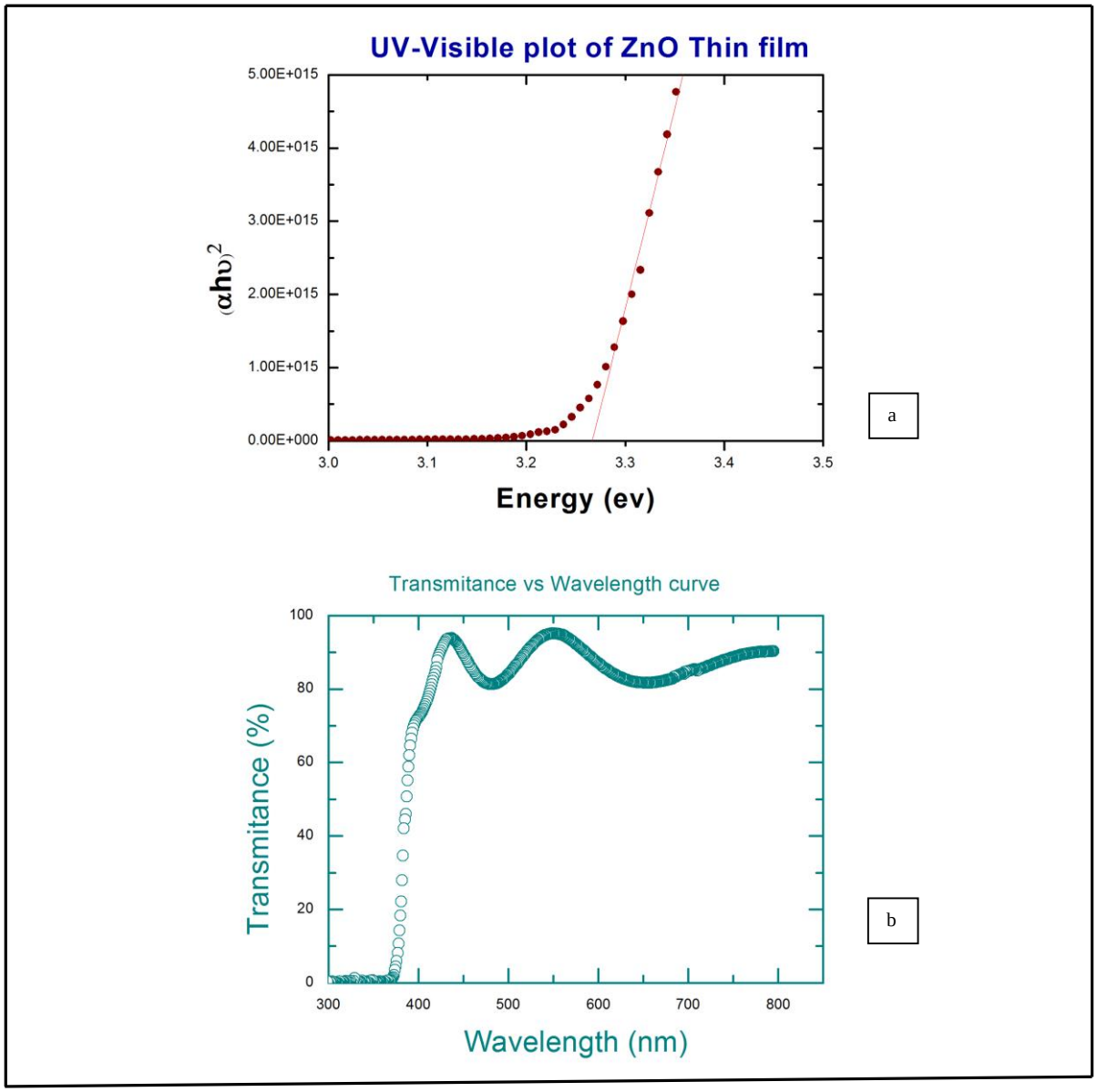


Figure 6.1.3 a) Band gap calculation b) Transmittance Curve

6.2. ZnO NANOWIRES

In this section, ZnO nanowires grown by hydrothermal method are studied in detail for their morphology and crystal structure. Further effect of precursor concentration, growth temperature,

growth time on morphology and crystallinity of ZnO nanowires put under discussion through XRD and FESEM results.

6.2.1. X-Ray Diffraction:

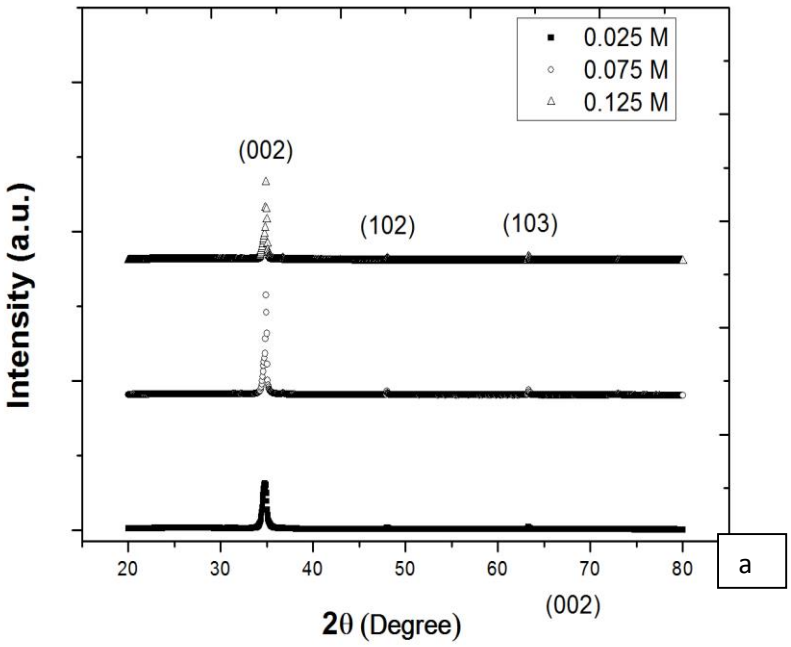
The X-ray diffraction data were collected on a Rigaku Ultima IV diffractometer using Cu K_{α}-radiation (λ=1.5418Å) over a range $20^0<\theta<80^0$ at operating voltage of 40 kV and operating current of 40 mA. In this section XRD pattern of nanowires for various concentration and growth temperature have been analyzed.

Varying Precursor Concentration

Maximum peak intensity is observed for 0.075 M solution, showing that at this molar concentration well aligned nanowires are formed. New peaks are observed corresponding to the plane (102) and (103) with increased intensity on increase in temperature. From this observation it can be said that increment in precursor concentration in the solution causes rapid nucleation of ZnO molecules and due to rapid nucleation molecules doesn't have time to find the most relaxed state and hence other growth direction can also be seen.

Varying Growth Temperature

It is observed that on increasing the growth temperature peak intensity of (002) plane increases. This can be attributed to the availability of required energy to the molecules to align themselves at proper orientation. Appearance of new peaks is observed with increase in temperature showing effect of thermal distortion on the crystalline structure [6].



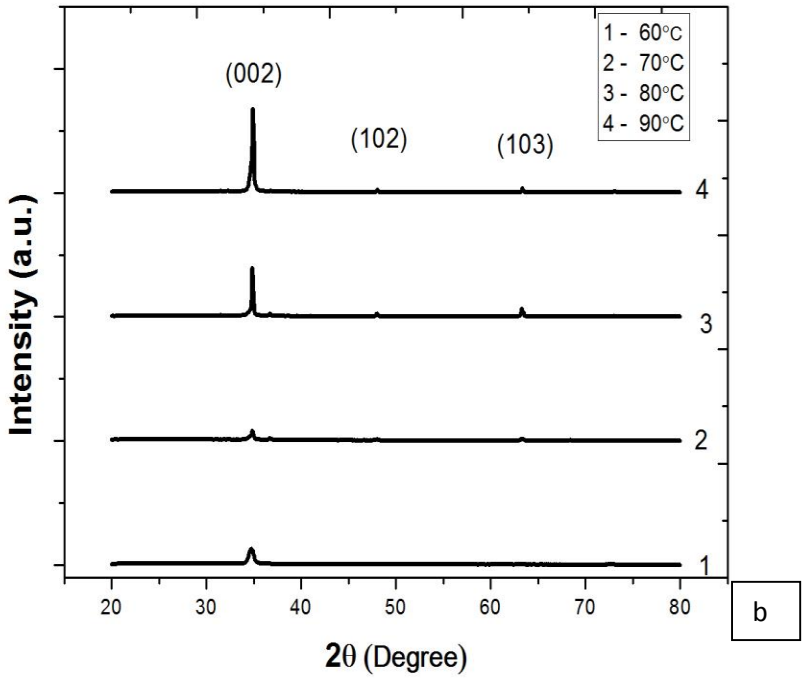


Figure 6.6.1 a) Variation with concentration b) Variation with temperature

6.2.2. Field Emission Scanning Electron Microscopy:

Varying Temperature

Temperature variation plays an important role in maintaining the aspect ratio. Aspect ratio is determined by relative growth of polar and non-polar surfaces. It increases with increase in temperature with maximum obtained at 90ºC.

At low temperature mobility and diffusion length of ions on the substrate is very low, which ceases the movement of ions and hence large nuclei are formed reducing the density of nanowires. At an increased temperature mobility and diffusion length is large enough to reach the site of already grown nanowires resulting in lower density [6][11].

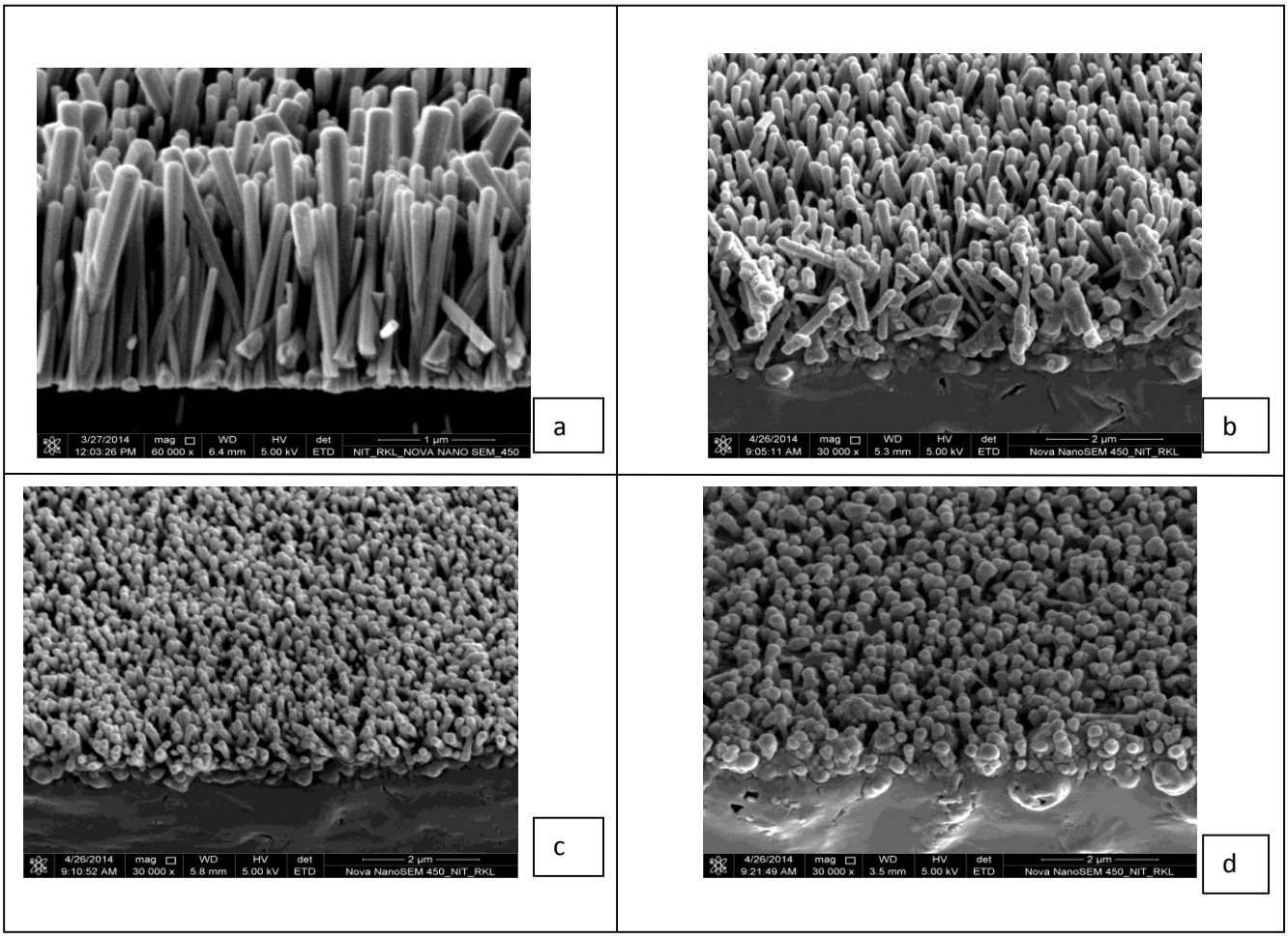
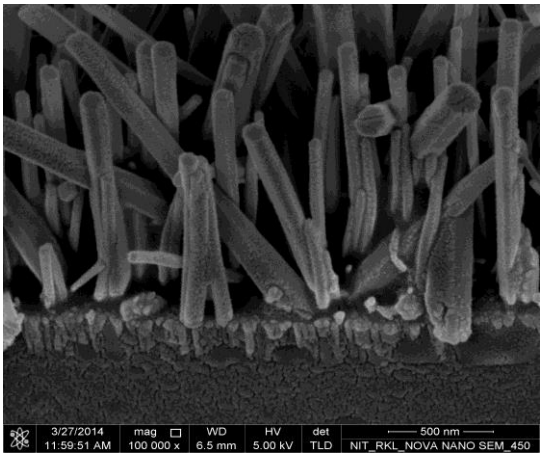


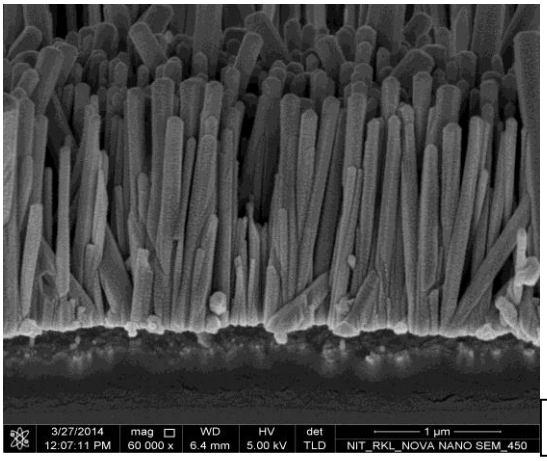
Figure 6.2.2 (I) Change in surface morphology of ZnO nanowires for with variation in growth temperature a) T= 90ºC b) T= 80ºC c) T= 70ºC d) T= 60ºC

Varying Precursor Concentration

When the precursor concentration in the solution increases, the nucleation of ZnO is so rapid that many ZnO nuclei form in the initial stage. These nuclei may aggregate together due to excess saturation. Also the chemical potential inside the solution body increases with increase in zinc concentration. This increased zinc chemical potential inside the solution can be balanced by generation of more nucleation sites on the substrate surface, and therefore, the density of ZnO NWs will increase. If the zinc concentration is further increased, the density of ZnO NWs remains approximately steady with a slight tendency to decrease. After saturation density more arrived ions will not contribute to the new nucleation sites but will dissolve into the solution, hence density will be constant [13] [11].



a



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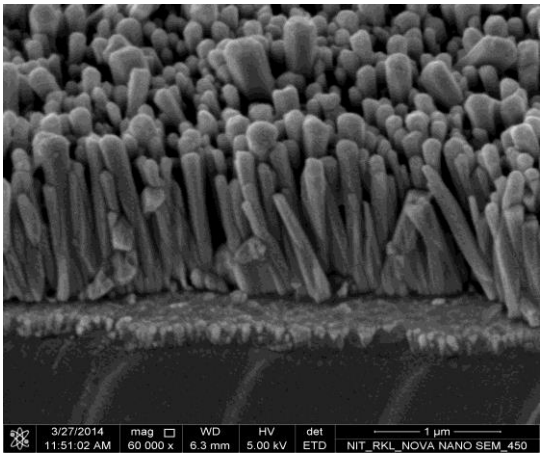


c

Figure 6.2.2 (II) Change in surface morphology with change in precursor concentration

a) Concentration = 0.025 M
b) Concentration = 0.075 M
c) Concentration = 0.125 M

6.2.3 UV Detection Property of ZnO nanowires

UV sensing property of ZnO nanowires have been studied by analysing I-V curve for both uncoated nanowires and Poly(vinyl alcohol) coated nanowires. It is observed that current increases with increase in bias voltage for both coated and uncoated nanowires that for coated ZnO nanowires but increment for coated nanowire is more significant. Polymer coated nanowires have more sensitivity, faster response and better recovery time than uncoated nanowires.

Idea for the PVA coating came from storage of food in food industries. Generally, PVA is used to create a barrier for the oxygen ensuring proper storage. In UV detection mechanism, it reduces the width of depletion layer of oxygen on the surface of nanowire and hence reduces the surface carrier trapping of the carriers. Decay in photocurrent due to photocurrent relaxation decreases. During the steady illumination decrease in photocurrent for PVA coated nanowire is less than for as grown nanowires. Because of the thin depletion layer there is a fast recovery of photocurrent in coated nanowires [17].

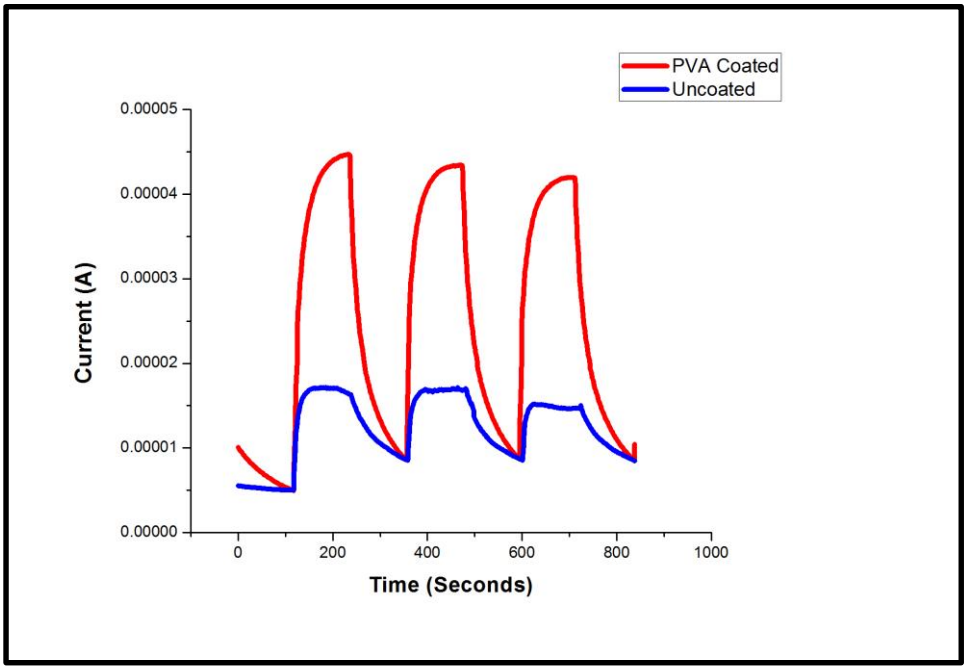
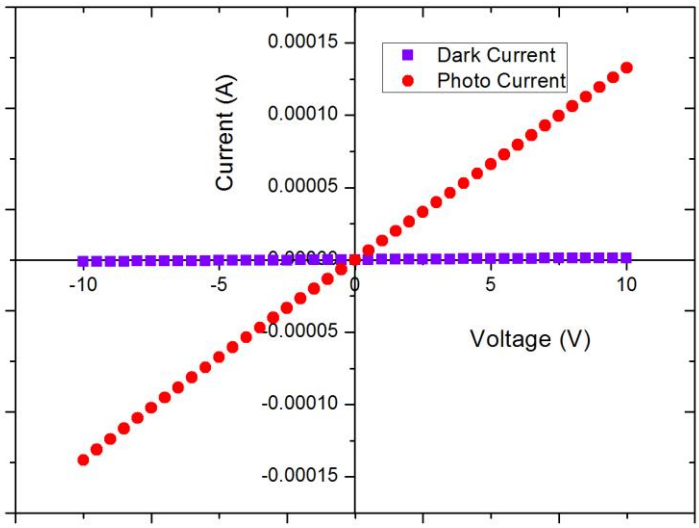


Figure 6.2.3 (II) I-T Characteristics



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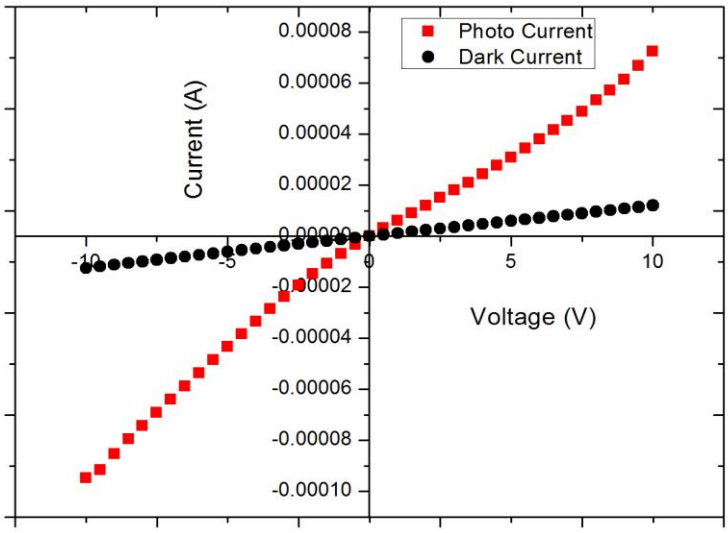

b

Figure 6.2.3 *a) I-V Characteristics of coated ZnO nanowires*

b) I-V Characteristics of uncoated ZnO nanowires

- Increment in photocurrent for coated surface in more significant -
    - Increment in uncoated surface ~ 18 times
    - Increment in coated surface ~ 50 times
- Decrement in photocurrent for long time UV exposure -
    - Coated ~ 3.10 %
    - Uncoated ~ 13.42 %

Conclusion

Thin Film

In this review, ZnO thin film grown by RF magnetron sputtering is studied for its crystallinity, crystallite size, thickness, surface morphology and band gap. It is observed that deposited thin film have high crystallinity with characteristic peak at 2θ value of 34.91 Degree. Inter-planer distance for the planes where most of the ZnO atoms are arranged is (d) 2.6 Aº. It has crystallite size of around 14 nm. Thickness of film is found to be 796.04 nm and band gap is 3.26 eV. Transmittance curve shows transparency of the ZnO film for UV and visible light.

Nanowire

Zinc oxide nanowires have been grown on seeded crystalline Zinc Oxide layer deposited on Glass Substrate by Hydrothermal Method using Hexamethylenetetraamine (HMT) and Zinc Nitrate as precursor solution, resulting in well aligned nanowires. It can also be concluded that seeded zinc oxide layer is critical for the growth of nanowires. Nanowires morphology, length and density is significantly affected by precursor concentration, growth temperature and growth time. Due to wide band gap of ZnO which falls in UV range, ZnO nanowires can be used as UV photodetector. To enhance the UV absorption ability and electron transport property, surface functionalization is carried out using Poly(vinyl alcohol). From I-V characteristics it is found that functionalized nanowires shows better switching action and large deviation of photo current from dark current. This behaviour of ZnO nanowires shows their suitability for commercial UV photodetector which can be manufactured using Schottky contact for better response time.

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